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# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improved Release of Curing Agents from Molecular Sieves

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignee of SANTO GIAMBRA and DONALD JAMES WAYTHOMAS), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the improved release of active chemical curing agents previously adsorbed in crystalline zeolitic molecular sieves. The curing agents are released in a reaction zone at elevated temperatures where they serve as accelerators or catalysts for the curing of organic resins such as the epoxy, polyester, polysiloxane, polysiloxane-epoxy, phenolic, polyethylene glycol-dimethacrylate, and the chemically cross-linked polyethylene type. Resins are useful in the manufacture of potted electrical components, adhesives, coatings, sealants or impregnated tapes. The invention is also applicable to the curing of curable elastomers such as rubber formulations. The many end uses of rubber are well known.

Various methods have been proposed for controlled release of curing agents from molecular sieves. For example, water may be employed to displace the active agent in a reaction zone. However, epoxy resins find important uses in electrical service, and the presence of residual water in such resins may have deleterious effects on the electrical properties of the cured, finished product. Furthermore, water is so strongly adsorbed by molecular sieves that the curing agent is rapidly released. This may not be desirable or convenient in all epoxy and rubber systems.

Another previously proposed method of releasing curing agents from molecular sieves is by coadsorption of a polar material. The latter facilitates a lower release or desorption temperature for the active agent than would be required in the absence of the polar material. However, the disadvantages of this method include the necessity of first coadsorbing the active agent and the polar material in the molecular sieve. That is, a limited amount of curing agent can be accommodated by the molecular sieve due to the need for coadsorption of the release material. As a result both the curing agent and the release material are not present in as large amounts as may actually be needed under some processing conditions. Practical considerations often limit the amount of release agent which can be coadsorbed along with the curing agent. Accordingly, the sieve containing both the curing agent and the release material must often be heated to above about 160° C. for release of the active agent, whereas many systems favor or require lower curing temperatures, as for example, where epoxy resins are used to encapsulate delicate, temperature-sensitive electronic components or where the resins are cast in large masses.

It should be recognized that one important advantage of all chemical-loaded molecular sieves in resin formulations is that extended pot lives may be achieved in one package. The conventional epoxy systems cannot be premixed if extended storage stability is desired; hence, very often "two-package" systems are required to provide the extended pot life necessary for packaging. That is, if the accelerator or catalyst were mixed directly with the curable formulation, the reaction would proceed almost immediately and it would be useless to attempt to package the mixture for processing at a later date.

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While resin formulations are desirably stored at ambient temperature and then heated when curing is desired, rubber formulations are usually prepared at a first elevated temperature and then subjected to various stages of processing such as extruding and molding. Molecular sieves provide a means for holding the curing agent intact and inactive during these preliminary processing stages, so that a long scorch time is achieved. On heating to a second further elevated temperature the curing agent is released from the molecular sieve for participation in a reaction, so that a short cure time is realized.

An object of this invention is to provide an improved method for obtaining effective release of adsorbed curing agents from molecular sieves.

Another object is to provide an improved method for releasing adsorbed curing agents for organic resin and rubber formulations, which method does not involve the use of water.

Still another object is to provide a water-free method for curing resin and rubber formulations at lower temperatures than heretofore possible.

Other objects are to provide improved resin and rubber formulations which can be heat cured at lower temperatures than heretofore possible.

It has been discovered that the aforementioned problems may be overcome and the objects realized by providing a method for curing a resin or a curable elastomer in which a curing agent, is adsorbed within the inner adsorption region of a dehydrated crystalline zeolitic molecular sieve. The selected curable resin or elastomer, the curing agent-loaded molecular sieve, and a release agent are provided in a reaction zone at below curing temperature. The release agent is a substantially anhydrous organic hydroxyl-containing compound, having a critical dimension no larger than the apparent pore size of the molecular sieve, as for example, alcohols, diols, triols, polyols, phenols, organic acids, hydroxy glycol ethers, ketones (as the enol form), and alkanolamines of the class  $R_3N$ , where at least one R has an OH group and the remainder are alkyl, such as triethanolamine and N,N-dimethyl ethanolamine. The expression "hydroxyl-containing compound" as employed in the present specification defines compounds having an  $-OH$  group and also compounds having a  $-C=O$  group.



The release agent is not appreciably adsorbed by the molecular sieve at below curing temperature. When curing is desired, the reaction zone is heated to a preselected suitable curing temperature, normally at least about 75° C. At the selected temperature, the release agent begins to occupy the adsorption sites of the

molecular sieve and thus displaces the curing agent from the molecular sieve. That is, the selectivity of the molecular sieve for the release agent apparently increases when the reaction zone is heated to the curing temperature. The released curing agent then reacts with the selected curable member.

The release agent must be of sufficiently small molecular size to pass into the inner adsorption region of the molecular sieve, and displace the curing agent at the desired curing temperature. Since the apparent pore size of the largest known crystalline zeolitic molecular sieve is about 10 Angstrom units, this value approximately represents the critical dimension of the largest release agent useable in the present invention.

Examples of alcohols suitable as the release agent include methanol, ethanol, propanol and butanol. Satisfactory organic acids include acetic acid, oxalic acid and maleic acid. Diols are particularly suitable, as for example ethylene glycol, 1,3 propylene glycol, 1,4 butanediol, and 1,5 pentanediol, and hexylene glycol. Satisfactory triols include glycerol and 1,2,6 hexanetriol. Glycol ethers found useful include CELLOSOLVES (CELLOSOLVE is a Trade Mark) and CARBITOLS, (CARBITOL is a Trade Mark) as manufactured and sold by Union Carbide Corporation, 270 Park Avenue, New York City. Polyglycols found useful include polypropylene glycols and polyethylene glycols.

In the case of alcohols, hydroxy glycol ethers, diols, triols, organic acids, enol forming ketones and polypropylene glycols, compounds of molecular weights below about 450 are suitable as the release agent. However, when polyethylene glycols are used, the molecular weight can be as high as about 4000, particularly if the higher curing temperatures are employed. Particularly preferred release agents for epoxy resin formulations are hexylene glycol (mol. wt. 118), glycerol (mol. wt. 92) a polypropylene glycol of about 150 average mol. wt., and a polyethylene glycol of about 400 average mol. wt.

Materials of large critical dimension such as refined castor oil (largely glyceryl triricinoleate) have not given consistently satisfactory results in that no cure was obtained under the test conditions and was not deemed to be acceptable for commercial use. It was found that castor oil is not adsorbed by sodium zeolite X, or at most only very slowly, whereas a polyethylene glycol of about 600 average molecular weight is readily adsorbed on this molecular sieve with definite evolution of heat. In the case of castor oil, it is believed that negligible adsorption because of its large critical dimension was the primary factor contributing to unsatisfactory release of the curing agent.

The organic hydroxyl-containing release agents must be substantially anhydrous and

should preferably be dried to less than about 0.5 wgt.-%  $H_2O$  before incorporation in the epoxy resin or rubber formulations to avoid premature release effects or foaming. This pre-drying step may be accomplished by any known desiccating means. One particularly effective method involves the use of molecular sieve adsorbents such as potassium zeolite A (Linde Type 3A—LINDE is a Trade Mark), sodium zeolite A (Linde Type 4A), and calcium zeolite A (Linde Type 5A) Molecular Sieves. These materials are characterized by high adsorption capacity for water from liquids containing any traces of water, and can effectively dry polar liquids such as alcohols and glycols.

It appears that the amount of hydroxyl release agent present will affect the pot life and curing characteristics. Adjustment of the hydroxyl release agent concentration, therefore, should provide a convenient means for controlling the properties of resin formulations. Excellent results have been obtained with a release agent-curing agent weight ratio of 1. For example, with zeolite X containing 20 wgt.-% diethylene triamine as the curing agent, it is preferred to use 1 part by weight release agent per 5 parts by weight of the curing agent-molecular sieve. If less release agent is used, the pot life will be improved at the expense of cure time, while the reverse is true if more release agent is employed.

The term "zeolite," in general, refers to a group of naturally occurring and synthetic hydrated metal aluminosilicates, many of which are crystalline in structure. There are, however, significant differences between the various synthetic and physical properties such as x-ray powder diffraction patterns.

The structure of crystalline zeolitic molecular sieves may be described as an open three-dimensional framework of  $SiO_4$  and  $AlO_4$  tetrahedra. The tetrahedra are cross-linked by the sharing of oxygen atoms, so that the ratio of oxygen atoms to the total of the aluminum and silicon atoms is equal to two, or  $O/(Al+Si)=2$ . The negative electrovalence of tetrahedra containing aluminum is balanced by the inclusion within the crystal of cations, for example, alkali metal and alkaline earth metal ions such as sodium, potassium, calcium and magnesium ions. One cation may be exchanged for another by ion-exchange techniques.

The zeolites may be activated by driving off at least a portion of the water of hydration. The space remaining in the crystals after activation is available for adsorption of adsorbate molecules having a size, shape and energy which permits entry of the adsorbate molecules into the pores of the molecular sieves. Activation may be conveniently carried out by heating the zeolite under reduced pressure until the water is removed. The temperature required depends upon the properties of

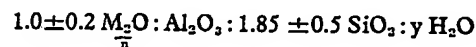
the particular zeolite. In general, when crystalline zeolitic molecular sieves are to be used for adsorption of curing agents for use in the present invention, such sieves should preferably be fully activated or nearly so, that is, they should contain less than about 2 weight per cent water in order to obtain the maximum advantage from the use of the active chemical-loaded molecular sieve.

The zeolites occur as agglomerates of fine crystals or are synthesized as fine powders and are preferably tableted or pelletized for large-scale adsorption uses. Pelletizing methods are known which are very satisfactory because the sorptive character of the zeolite, both with regard to selectivity and capacity, remains essentially unchanged.

Any type of crystalline zeolitic molecular sieve may be employed in the present method according to this invention. The selection of the particular sieve to be used will depend on factors such as the maximum critical dimensions of the curing agent molecule and release agent molecule to be employed, the apparent pore size of the molecular sieve, and the nature of the reaction within the reaction zone. For example, the pores must be at least large enough to receive the desired molecules. The term, "apparent pore size," as used herein, may be defined as the maximum critical dimension of the largest molecular species which is adsorbed by the zeolitic molecular sieve in question under normal conditions. The apparent pore size will always be larger than the effective pore diameter, which may be defined as the free diameter of the appropriate silicate ring in the zeolite structure.

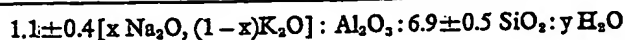
Among the naturally occurring crystalline zeolitic molecular sieves are chabazite, erionite, faujasite, analcite, clinoptilolite and mordenite. The natural materials are adequately described in the chemical art. Synthetic zeolitic molecular sieves include zeolites A, D, R, T, X, Y, L and S. Zeolites such as types X, Y, L and faujasite are particularly useful because of their relatively large pore sizes.

Zeolite A is a crystalline zeolitic molecular sieve which may be represented by the formula:



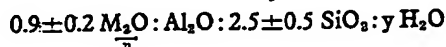
wherein M represents a metal, n is the valence of M, and y may have any value up to about 6. The as-synthesized zeolite A contains primarily sodium ions and is designated sodium zeolite A. Zeolite A is described in more detail in British Patent Specification No. 777,232.

Zeolite T is a synthetic crystalline zeolitic molecular sieve whose composition may be expressed in terms of oxide mole ratios as follows:



wherein "x" is any value from about 0.1 to about 0.8 and "y" is any value from about zero to about 8. Further characterization of zeolite T by means of x-ray diffraction techniques is described in British Patent Specification No. 912,936.

Zeolite X is a synthetic crystalline zeolitic molecular sieve which may be represented by the formula:



wherein M represents a metal, particularly alkali and alkaline earth metals, n is the valence of M, and y may have any value up to about 8 depending on the identity of M and the degree of hydration of the crystalline zeolite. Sodium zeolite X has an apparent pore size of about 10 Angstrom units. Zeolite X, its x-ray diffraction pattern, its properties, and methods for its preparation are described in detail in British Patent Specification No. 777,233.

Zeolite Y is described and claimed in British Patent Specification No. 909,266.

Zeolite L is described and claimed in British Patent Specification No. 909,264.

Zeolite R is described and claimed in British Patent Specification No. 841,812.

Zeolite S is described and claimed in British Patent Specification No. 909,265.

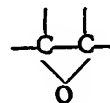
Zeolite D is described and claimed in British Patent Specification No. 868,846.

The molecular sieve may be internally loaded with a curing agent by placing in a vacuum desiccator a weighed portion of activated crystalline zeolite molecular sieve in a container which exposes a substantial surface. The compound to be adsorbed is then placed within the desiccator in another communicating container. A vacuum is placed on the desiccator and the system is then sealed. The rate of adsorption is a direct function of the vapor pressure of the compound being loaded. If the rate of adsorption is too slow at room temperature, the desiccator may be subjected to elevated temperatures. The weight per cent loading is calculated from the weight increase of the molecular sieve. If the curing agent is a solid, it may be adsorbed by intimate mixing or blending with the molecular sieve. Again, heating either during or after blending accelerates the adsorption. If the material does not possess appreciable vapor pressure, it may be adsorbed by the molecular sieve from a liquid solution wherein the solvent is not adsorbed. Also, loading may be achieved by controlled contact of a liquid curing agent and the activated molecular sieve.

The amount of curing agent or catalyst loaded on the molecular sieve is generally in

the range of about 0.001 to 25% by weight based on the weight of the sieve. At different weight per cent loadings there is no substantial difference in performance of the loaded sieve for its intended purpose.

The present invention may be employed for the curing of natural and synthetic resins as for example the epoxy type containing at least one of the following reactive groups in their molecule:



The epoxy resins may be saturated or unsaturated, aliphatic cycloaliphatic, aromatic or heterocyclic and may be substituted with non-interfering substituents. The epoxy may be either present as a terminal or interior group.

Illustrative of the monomeric type epoxy resins are the following: vinyl cyclohexane dioxide, epoxidized soybean oil, butadiene dioxide, 1,4-bis(epoxypropoxy)benzene, 1,3-bis(2,3-epoxypropoxy)cyclohexane, 4,4-bis(2-hydroxy-3,4-epoxybutoxy)-diphenyldimethylmethane, 1,3-bis(4,5-epoxypentoxo)-5-chlorobenzene, 1,4-bis(3,4-epoxybutoxy)-2-chlorocyclohexane, 1,3-bis(2-hydroxy-3,4-epoxybutoxy)-benzene, 1,4-bis(2-hydroxy-4,5-epoxypentoxo)benzene, 1,2,5,6-diepoxy-3-hexane, 1,2,5,6-diepoxyhexane and 1,2,3,4-tetra(2-hydroxy-3,4-epoxybutoxy)-butane. Other compounds of this type include the glycidyl polyethers of polyhydric phenols obtained by reacting mixtures containing a molar amount of a polyhydric phenol with a stoichiometric excess, i.e., 3 to 6 moles per each phenolic hydroxy group, of an epichlorohydrin in an alkaline medium, and also polyglycidyl esters, such as are prepared by reacting an epichlorohydrin with a salt of a polybasic acid.

Examples of the polymeric type epoxy resins include the glycidyl polyethers of polyhydric phenols obtained by reacting, preferably in an alkaline medium, a polyhydric phenol and 1-2 moles of an epichlorohydrin per each phenolic hydroxyl group. Illustrative of this particular type compound is the polyether obtained in reacting 1 mole of bis(4-hydroxyphenyl)dimethylmethane with 1.5 moles of epichlorohydrin in the presence of an alkaline catalyst.

Among the curing agents suitable for curing epoxy resin formulations and which have been loaded into activated molecular sieves are polyamines such as diethylenetriamine, triethylenetetramine, m-phenylenediamine, and ethylenediamine. Other suitable amine curing agents are triethanolamine, N,N-

dimethylethanolamine, benzyldimethylamine, and triethylamine.

The present invention may also be employed for curing other resin formulations such as the unsaturated polyester resins. These are formed by combining the reaction product of a dihydric alcohol, such as alkylene glycols and an unsaturated dibasic acid, such as maleic acid, with a polymerizable monomer such styrene in the presence of a peroxide curing agent. Suitable peroxides which can be adsorbed on molecular sieves include tertiary butyl hydroperoxide, ditertiary butyl peroxide and dicumyl peroxide. Cross-linking takes place between the double bonds in the polyester and the styrene monomer to form an insoluble, infusible resin.

Another resin curable by the invention is a dimethacrylate ester of a glycol such as polyethylene glycol, in homogeneous mixture with polyvinyl chloride. The plastisol when cured with a peroxide catalyst is extremely hard and strong.

Polysiloxane resins may be cured by amines such as diethanolamine. Polysiloxane-epoxy resins can be cured by the same agents as previously listed for epoxy resins. Phenolic resins are cured by, for example, ammonia and formaldehyde, or hexamethylene tetramine. The chemically cross-linked polyethylene resins are curable by peroxide compounds such as dicumyl peroxide, ditertiary butyl peroxide.

The present invention may be employed for the curing of various types of rubber formulations. The adsorbed curing agent may be sulfur, a peroxide such as dicumyl peroxide, a polyamine such as triethylene-tetramine and other suitable cross-linking agents. An adsorbed accelerator may be the "primary" type which actually catalyzes the formation of sulfur radicals or the "secondary" type (commonly called the "activator") which increases the activity of the primary accelerator. Alternatively, the adsorbed curing agent may be a combination of primary and secondary type accelerators.

The rubber formulation may, for example, be the neoprene type, which is the generic term applied to the group of synthetic elastomers based on the polymers of chloroprene, that is, 2-chlorobutadiene-1,3. Two particularly important classes of polychloroprene polymers are designated Type G neoprenes and Type W neoprenes. Type G neoprenes are sulfur-modified chloroprene-based synthetic elastomers and Type W neoprenes are stabilized non-sulfur modified chloroprene-based synthetic elastomers. Suitable neoprene accelerators include, dihydroxy benzenes, such as pyrocatechol and resorcinol; alkyl-substituted dihydroxybenzenes such as ethylcatechol and ethyl resorcinol; and hydroxy-substituted benzoic acids, such as

salicylic acid and p-hydroxy benzoic acid. Other neoprene accelerators are well known to the art, and a more complete listing can be found in British Patent Specification No. 909,267.

The rubber formulation may also be the butyl type made by copolymerizing an isolefin, usually isobutylene, with a minor proportion of a multi-olefinic unsaturate having from 4 to 14 carbon atoms per molecule. The isoolefins used generally have from 4 to 7 carbon atoms, and such isomonoolefins as isobutylenes or ethylmethylethylene are preferred. The multi-olefinic unsaturate usually is an aliphatic conjugated diolefin having from 4 to 6 carbon atoms, and is preferably isoprene or butadiene. Suitable accelerators for butyl rubber curing include strong acids such as HCl, HBr, HI and halogen-substituted organic acids. Other suitable accelerators are unsaturated organic halides as 1,4-dichlorobutene, 2-chloropropene, 2-bromopropene and 2-iodopropene; also acyl halides such as benzoyl chloride; and alkyl benzenes such as alphaalphaalpha trichlorotoluene. The incorporation of curing accelerators in molecular sieves for butyl rubber curing is described more completely in British Patent Specification No. 912,937.

The present invention may also be employed for the curing of other rubber formulations, as for example the Buna (BUNA is a Trade Mark) or SBR type. Buna rubber is a synthetic rubber prepared by the polymerisation of butadiene and comprises about 75% butadiene, styrene being the other main constituent. Suitable well-known accelerators for Buna rubber include thiurams, arylamines, alkylarylamines and thioureas. Other examples are piperidine, diethylamine, and di-n-butylamine.

Natural rubbers are also amenable to this novel method as are other synthetics such as polyacrylates, polyisoprene, polybutadiene, ethylenepropylene rubber, butadiene acrylonitrile copolymers, butadiene acrylic ester copolymers, and silicone rubber.

It should be understood that this invention may not be employed where the release agent is reactive with a functional group in the curable resin or elastomer at below the curing temperature.

In carrying out the present method, the particular organic resin or rubber formulation, the curing agent-containing molecular sieve, and a predetermined amount of release agent are combined by, for example, standard blending and mixing methods. While the mixed formulation is maintained at about processing temperature, the release agent has little or no effect on the curing agent-containing molecular sieve. Accordingly, while the system is stored for relatively long periods of time at about room temperature, little or no interaction occurs therein and the viscosity of

the formulation increases at a very small rate. When curing is desired, the formulation is heated by any convenient means to achieve the desired cure temperature. This is above the temperature at which the release agent begins to modify the affinity of the molecular sieve for, and eventually to displace the active agent from the molecular sieve. The curing agent is released and the crosslinking mechanism proceeds. In practicing the method of the invention for the majority of epoxy resin formulations, a useful range of curing temperatures is from about 75° C. to about 175° C.; however, in special instances processing requirements may call for rapid cures at higher temperatures, such as around 200° C. For rubber formulations, curing temperatures in the range of about 135° C. to 200° C. are normally employed by the instant method.

A series of experiments were performed in which the effectiveness of various release agents in bringing out satisfactory curing characteristics without loss of good viscosity-time characteristics ("pot-life") was studied. The relative hardness or resistance to localized indentation of cured epoxy resin samples was evaluated by the Barcol hardness method commonly used for epoxy and polyester resins. The Barcol "Impressor" hardness tester (No. 935) employs a hardened indenter with a dial scale calibrated against an aluminum disc of 87-89 hardness; the peak reading of the scale obtained when the indenter is forced at right angles into the resin film is taken as the hardness value of that film. Viscosity-time behavior was followed by measurements of the initial viscosity and subsequent periodic sampling, in some cases over a period of weeks or months. Viscosity measurements were made with a Brookfield viscosimeter at 25° C. The Brookfield viscosimeter gives a direct determination of viscosity on the basis of measurement of the torque imposed on a calibrated spring by a spindle rotating at constant speed. The Model RVF used here permitted measurements at 4 speeds (2, 4, 10, and 20 r.p.m.) over a viscosity range of 0-2,000,000 centipoises.

#### EXAMPLE 1.

Diethylenetriamine is a well-known curing agent for epoxy resins; 20 grams of this polyamine were loaded into the inner adsorption region of 80 grams of zeolite X. A mixture was prepared consisting of 48.8 grams of the diglycidyl ether of bisphenol A (a liquid epoxy resin), 5.25 grams of

anhydrous glycerol, and 26.25 grams of the 20 wt.-% diethylenetriamine-loaded molecular sieve. This mixture formed a thixotropic resinous mass, and a sample portion placed in an oven at 100° C. cured to a hard resin in less than ten minutes. A second sample was placed under an infrared lamp at 82° C. and cured to a hard resin in eight minutes; this formulation, surprisingly enough, was still useable after two months storage at room temperature. In the absence of a release agent, adsorbed diethylenetriamine is not released from zeolite X at 100° C. in less than 10 minutes in an epoxy resin. In a control experiment employing the same temperature conditions and 10.8 parts of unloaded diethylenetriamine per 100 parts of the same liquid epoxy resin, the latter cured in five minutes; this formulation, however, had a pot life of only 30 minutes.

This experiment illustrates that when curing was desired, it was obtained almost as rapidly by release of the agent from a molecular sieve, as can be obtained when the agent is mixed directly with the epoxy resin. Moreover, the present invention permits packaging and storage of the formulation for long periods without appreciable curing whereas such storage is impossible if the curing agent is directly mixed in the formulation.

#### EXAMPLE 2.

Another mixture was prepared of 97.6 grams of the same liquid epoxy resin as in Example 1, 52.4 grams of 20 wt.-% diethylenetriamine-loaded zeolite X powder, and 10.5 grams anhydrous glycerol. The ingredients were thoroughly mixed and produced a pasty, thixotropic mass. During the curing step at 82° C., a sample of the resin did not change shape, i.e., did not flow when heated, thus demonstrating its thixotropic character. The uncured resin mass showed good storage stability, i.e., it retained its initial viscosity characteristics after two weeks at room temperature.

#### EXAMPLE 3.

Although some hydroxyl materials are known curing agents for epoxy-amine reactions, relatively high reaction temperatures above 200° C. are usually required. To determine whether a hydroxyl material such as glycerol might itself be entering into the crosslinking reaction even at the relatively low curing temperatures employed in the present method, the following lots of epoxy resin mixtures were prepared:

Ingredient	Lot*			
	Control	A	B	C
Diglycidyl ether of bis phenol A	10	10	10	10
Glycerol	—	1	—	1
20 wt-% diethylenetriamine-loaded zeolite X	—	—	5	5

\* Weights in grams.

After heating these four batches for 10 minutes at 100° C., only the resin from Lot C (containing diethylenetriamine - loaded molecular sieve and glycerol) had cured, thus demonstrating that neither the glycerol by itself (Lot A), or the amine-loaded zeolite X

by itself (Lot B) enters into the reaction at these temperatures.

#### EXAMPLE 4.

The following batches of epoxy resin mixtures incorporating dried hydroxylated materials were prepared:

Ingredient	Batch*			
	A	B	C	D
Diglycidyl ether phenol A	100	100	100	100
20 wt-% diethylenetriamine-loaded zeolite X	54	54	54	54
1,3 propylene glycol	10.8	—	—	—
1,4 butanediol	—	10.8	—	—
1,5 pentanediol	—	—	10.8	—
Castor oil	—	—	—	10.8

\* Weights in grams.

Samples of batches A, B and C cured in 10 minutes at 100° C., and in 5 minutes at 125° C. and 150° C. Samples of batch D did not cure even after 3 hours at 150° C. The Barcol hardness values of samples A, B and C after a 10-minute cure at 100° C. were 83, 83 and 85, respectively; after a 10-minute cure at 125° C. the values were 85, 87 and 87, respectively. The absence of cure in the sample of D is typical of the inability of over-size molecules to act as release agents because they cannot enter the molecular sieve pores and release the diethylenetriamine from the molecular sieve. Continued observation of the batches containing butanediol and pentanediol showed that these systems were room-temperature stable for longer than two months.

#### EXAMPLE 5.

A mixture was prepared consisting of 100 parts by weight of the same liquid epoxy resin as used in Example 1, 54 parts of 20 wt-% diethylenetriamine-loaded zeolite X and 10.8 parts of dried 2,3 butanediol, which contains secondary hydroxyl groups. Satisfactory cure of a sample was achieved after 15 minutes at 80° C. under an infrared lamp. This batch showed satisfactory viscosity stability after a two-week's storage period.

#### EXAMPLE 6.

A mixture was prepared consisting of 25 grams of the same liquid epoxy resin, 17.5 grams of 20 wt-% metaphenylenediamine-loaded zeolite X, and 3.5 grams of dried glycerol. These were mixed together at room temperature and the resulting mass was

thixotropic. A sample of this mixture cured in less than 30 minutes at 125° C. to a very hard maroon-colored solid; a control sample containing no glycerol release agent did not cure after three hours at 125° C.

#### EXAMPLE 7.

Nine separate epoxy resin mixtures were prepared, each containing 10.8 grams of a different hydroxyl-containing material (dried) along with 100 grams of the previously employed liquid epoxy resin and 54 grams of 20 wt.-% diethylenetriamine-loaded zeolite X. The hydroxyl-containing materials were four polyethylene glycols, dipropylene glycol, polypropylene glycol (150 average mol. wt.), hexylene glycol, 1,5 pentanediol and phenol. As Table I shows, samples of Batches A, G and H cured in 15 minutes at 100° C. Batches B, F, and G exhibited exceptionally good storage stability. Based on these data, a storage-life or "pot-life" of between four and six months is indicated.

#### EXAMPLE 8.

Three batches of epoxy resin were prepared; in addition to 1000 grams of the liquid epoxy resin and 540 grams of 20 wt.-% di-

ethylenetriamine-loaded zeolite X, one contained 108 grams of dried hexylene glycol. The second batch contained 108 grams of dried polyethylene glycol of about 400 molecular weight, and the third contained 108 grams of dried polypropylene glycol of 150 molecular weight. Curing tests were run on 5-gram samples of each of these mixtures. All samples were cured after 15 minutes at 125° C.; in curing tests at 150° and 175° C., all samples were cured in 5 minutes.

#### EXAMPLE 9.

A coal tar-epoxy resin formulation was prepared from the following ingredients: the previously used liquid epoxy resin, 100 parts; liquid coal tar, 85 parts; 20 wt.-% diethylenetriamine-loaded zeolite X, 54 parts; hexylene glycol, 11 parts. Satisfactory cure of a sample was obtained in 10 minutes at 163° C. in an oven, and in 5 minutes when heated with a gas flame, the resin being covered by aluminum foil to prevent surface ignition. This mixture exhibited extended pot-life. The Brookfield viscosity values originally (after initial mixing) and after 30 days were 40,000 and 36,000 centipoises, respectively.



TABLE I  
The Effect of Hydroxyl Release Agents of Varying Molecular Weight  
Upon the Stability and Cure of an Epoxy Resin

Ingredients	A	B	C	D	E	F	G	H	I
Diglycidyl ether of bis phenol A	100	100	100	100	100	100	100	100	100
20 wt. % diethylenetriamine-loaded zeolite X	54	54	54	54	54	54	54	54	54
Polyethylene glycol (Ave. mol. wt. 200)	10.8								
Polyethylene glycol (Ave. mol. wt. 400)		10.8							
Polyethylene glycol (Ave. mol. wt. 600)			10.8						
Polyethylene glycol (Ave. mol. wt. 1000)				10.8					
Dipropylene glycol					10.8				
Polypropylene glycol (Ave. mol. wt. 150)						10.8			
Hexylene glycol							10.8	10.8	10.8
1,5-Pentanediol									
Phenol									
15 Min. at 100° C.	Cure	N.C.	N.C.	N.C.	N.C.	N.C.	Cure	Cure	N.C.
15 Min. at 163° C.	Cure	Cure	Cure	Cure	Cure	Cure	Cure	Cure	Cure
Brookfield Viscosity at 25° C., Centipoises									
Original (4 RPM)	10,000	10,000	15,000	17,500	5,000	10,000	10,000	35,000	15,000
1 Day (4 RPM)	15,000	25,000	35,000	40,000	20,000	20,000	15,000	100,000	30,000
2 Days (4 RPM)	20,000	25,000	40,000	60,000	20,000	20,000	20,000	115,000	260,000
5 Days (4 RPM)	50,000	30,000	40,000	70,000	35,000	25,000	20,000	150,000	>2MM*
12 Days (4 RPM)	60,000	40,000	55,000	45,000	50,000	30,000	25,000	180,000	—
5 Weeks (4 RPM)	400,000	50,000	30,000	40,000	125,000	35,000	25,000	265,000	—

\*MM signifies a million.

## EXAMPLE 10.

A proposed commercial use required an epoxy resin formulation which could be applied on glass tape. It was required that the epoxy-impregnated tape be stable and uncured for at least 30 days at room temperature. Three epoxy compositions were prepared comprising blends of solid and liquid types based on the diglycidyl ether of bis phenol A. These epoxy resin compositions were mixed in formulations containing 20 wt.-% diethylenetriamine-loaded zeolite X, and dried 1,5 pentanediol as a release agent along with dried acetone to reduce the viscosity. These formulations were applied to 18-mil thick glass tape by a dipping method. The solvent was flashed off and the tapes rolled and placed in sealed containers. After a two-week storage period at room temperature, these tapes remained stable and curable. Samples of each tape cured at 100° C. after 15 minutes.

It is surprising that the previously described rapid-cure epoxy systems have good viscosity stability, since they contain rather viscous, large molecular weight materials acting as release agents. While extended pot-life in terms of weeks or months have been described herein, it should be recognized that a pot-life of even a few hours is all that is needed in certain industrial systems. Also, certain applications may require sufficient pot-

life at a temperature between ambient and curing temperatures.

## EXAMPLE 11.

Two mixtures were prepared, one containing 100 parts of the epoxy resin, 54 parts of 20 wt.-% diethylenetriamine-loaded zeolite X, and 10.8 parts of polypropylene glycol (150 average mol. wt.) as release agent, and another containing the same except that 10.8 parts of polypropylene glycol (425 average mol. wt.) were used as release agent. Steel plates (1" x 2" size) were heated to approximately 400° F. When the above two mixtures were applied as coatings to the heated plates, satisfactory cures were obtained in about 6 and 10 seconds, respectively, after which the specimens were quenched in a cold water bath. Examination showed the coatings to be relatively free of pinholes or foaming, and without evidence of the charring previously observed when higher curing temperatures (440—460° F. were attempted.

## EXAMPLE 12.

A basic recipe of 100 parts of the diglycidyl ether of bis phenol A liquid, 80 parts hexahydrophthalic anhydride, and 12.6 parts of 15 wt.-% dimethylethanolamine on zeolite X was prepared. Three hydroxyl-containing release agents (1.8 parts were added to separate samples, and the following results were obtained:

	Release Agent		
	Polypropylene Glycol (ave. mol. wt. 150)	Hexylene Glycol	Polyethylene Glycol (ave. mol. wt. 400)
Gel time at 250° F., mins.	30	35	25
Viscosity Stability at 77° F., centipoises			
Original	3M*	2M*	3M*
4 days	12M*	8M*	8M*
7 days	13M*	8M*	16M*
14 days	32M*	18M*	26M*
1 month	820M*	390M*	1.4MM+

\*M means thousand; +MM means a million.

The basic recipe with pure dimethylamine, not adsorbed into a molecular sieve, has been found to gel at 77° F. in 3—4 hours. It is thus apparent that far superior pot lives were realized by use of the present invention.

## WHAT WE CLAIM IS:—

1. A mixture comprising (a) a curable organic resin or elastomer, (b) a crystalline zeolitic molecular sieve having adsorbed therein a curing agent, and (c) a release agent

which is a substantially anhydrous organic hydroxyl containing compound, as hereinbefore defined, having a critical dimension no larger than the apparent pore size of the crystalline zeolitic molecular sieve and which is not appreciably adsorbed by the molecular sieve below curing temperatures but adsorbable at the curing temperature acting to replace the curing agent, the release agent being such that it does not act as a curing agent for the resin or elastomer.

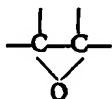
2. A mixture as claimed in claim 1 wherein the zeolitic molecular sieve is zeolite X, zeolite Y, zeolite L or faujasite.

3. A mixture as claimed in claim 1 or 2 wherein the release agent is a monohydric alcohol, diol, triol, polyol, phenol, organic acid, hydroxy glycol ether, ketone capable of enolising or alkanolamine having the general formula  $R_3N$  where at least one R has an OH group and the remainder are alkyl.

4. A mixture as claimed in any one of the preceding claims wherein the release agent contains less than 0.5 weight % of  $H_2O$ .

5. A mixture as claimed in any one of the preceding claims wherein the weight ratio of release agent to curing agent is 1.

6. A mixture as claimed in any one of the preceding claims wherein the curable material is a natural or synthetic epoxy resin containing at least one reactive group in their molecule having the formula:—



present as an interior or terminal group.

7. A mixture as claimed in claim 6 wherein the epoxy resin is aliphatic, cycloaliphatic, aromatic, or heterocyclic.

8. A mixture as claimed in claim 6 or 7 wherein the curing agent is a polyamine.

9. A mixture as claimed in claim 8 wherein the polyamine is diethylenetriamine, triethylenetetramine, m-phenylenediamine.

10. A mixture as claimed in any one of claims 1 to 5 wherein the curable material is an unsaturated polyester reaction product of a dihydric alcohol, an unsaturated dibasic acid and a polymerizable monomer.

11. A mixture as claimed in claim 10, wherein the curing agent is a peroxide.

12. A mixture as claimed in claim 11 wherein the peroxide is tertiary butyl hydroperoxide, ditertiary butyl peroxide or dicumyl peroxide.

13. A mixture as claimed in any one of claims 1 to 5, wherein the curable resin is a dimethacrylate glycol.

14. A mixture as claimed in claim 13 wherein the curing agent is a peroxide.

15. A mixture as claimed in any one of

claims 1 to 5, wherein the curable material is a polysiloxane resin.

16. A mixture as claimed in claim 15 wherein the curing agent is diethanolamine.

17. A mixture as claimed in any one of claims 1 to 5 wherein the curing material is a rubber formulation.

18. A mixture as claimed in claim 17 wherein the curing agent is a cross-linking agent.

19. A mixture as claimed in claim 18 wherein the cross-linking agent is sulfur, peroxide or a polyamine.

20. A mixture as claimed in claim 17 wherein the formulation is neoprene rubber.

21. A mixture as claimed in claim 20 wherein the neoprene rubber is Type G neoprene or Type W neoprene.

22. A mixture as claimed in claim 20 or 21 wherein the curing agent is a dihydroxy benzene, an alkyl-substituted dihydroxy benzene or a hydroxy substituted benzoic acid.

23. A mixture as claimed in claim 17 wherein the rubber formulation is butyl rubber.

24. A mixture as claimed in claim 23 wherein the curing agent is an unsaturated organic halide, a halogen substituted organic acid, acyl halide or an alkyl benzene.

25. A mixture as claimed in claim 17 wherein the rubber formulation is polyacrylate, polyisoprene, polybutadiene, silicone rubber or a synthetic rubber prepared by the polymerisation of butadiene.

26. A process for curing organic resins or elastomers comprising, providing in a reaction zone at below curing temperature, a mixture comprising: (1) a selected curable organic resin or elastomer, (2) a curing agent-containing crystalline zeolitic molecular sieve; and (3) a substantially anhydrous organic hydroxyl-containing (as hereinbefore defined) release agent having a critical dimension no larger than the apparent pore size of the molecular sieve and which is not appreciably adsorbed by the molecular sieve below the curing temperature but which is adsorbable at the curing temperature acting to replace the curing agent, the release agent being such that it does not act as a curing agent for the resin or elastomer; and storing said mixture until curing is desired; thereafter heating the reaction zone to a curing temperature thereby displacing the curing agent from the molecular sieve by the release agent and reacting the displaced curing agent with said selected curable member.

27. A method according to claim 26, in which the release agent is a monohydric alcohol, diol, triol, organic acid or ketone capable of enolising.

28. A method according to claim 26 in which the release agent is polyethylene glycol of maximum molecular weight 4000.

29. A method according to claim 26 in which the curable material is an epoxy resin and the release agent is hexylene glycol.
30. A method according to claim 26 in which the curable material is an epoxy resin and the release agent is glycerol.
31. A method according to claim 26 in which the curable material is an epoxy resin and the release agent is a polypropylene glycol of 150 average molecular weight.
32. A method according to claim 26 in which the curable material is an epoxy resin and the release agent is a polyethylene glycol of 400 average molecular weight.
33. A method according to claim 26 in which the curing agent is diethylenetriamine.
34. A method according to claim 26 in which the molecular sieve is zeolite X, Y, L or faujasite.
35. A mixture as claimed in claim 1 substantially as hereinbefore described in any one of the Examples.
36. A process as claimed in claim 26 substantially as described in any one of the Examples.

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